

COSMETIC COMPOSITIONFIELD OF INVENTION

5 The invention relates to a novel cosmetic composition, which has surprising occlusivity, which can be applied topically to the human body surface, especially the skin (including the mucosae), hair and nails.

10 BACKGROUND AND PRIOR ART

Hydrocarbons, such as petrolatum (also known as petroleum jelly or soft paraffin) have been used for many years for topical application to human skin for providing an occlusive film thereon to prevent water loss to the environment, thereby allowing water diffusing from the underlying tissues to accumulate in the stratum corneum. Petrolatum has also been used as an ingredient of skin care products, such as hand creams and lotions, and has also featured in hair grooming or conditioning products, particularly as a setting aid to maintain hair in a desired configuration.

25 It is, however, widely recognised that petrolatum possesses a relatively narrow spectrum of sensory or aesthetic properties. In particular, it can impart to the skin and hair an uncomfortable feeling of warmth, in addition to a sticky, waxy feel, and this has restricted its use to barrier products such as petrolatum itself and hand creams containing it, where a temporary functional protective film on the skin is desired, and to hair dressings such as pomades.

35 It is also recognised that petrolatum is derived from fossil fuels, whose supply is non-renewable.

In view of disadvantages such as those attributable to traditional petrolatum, there exists a need to locate an alternative occlusive product that has all the desirable attributes of emolliency and occlusivity of petrolatum, without serious negative subjective properties. Also, such an alternative product ideally should contain a major proportion of plant-derived material to suit environmental, ecological and personal health care needs.

DE 37 32 265 (Giulini Chemie GmbH) discloses gel compositions containing a magnesium aluminium hydroxide compound having a layered structure and a lipophilic organic compound which is liquid at room temperature.

However, we have shown that when the lipophilic organic compound used is a desired vegetable oil, the gel composition has negligible occlusivity.

We have further shown that when a gel composition comprising a layered double hydroxide and a vegetable oil additionally comprises a secondary thickener that is solid at room temperature, surprising occlusivity is achieved.

#### SUMMARY OF THE INVENTION

Accordingly the invention provides an occlusive gel composition comprising

(i) a layered double hydroxide having the general structure



where  
 A is a calcium, zinc or magnesium ion  
 B is an interlayer anion  
 y is a charge on the anion  
 x is 0.1 to 0.5

z is 0 to 100

providing that at least 50% of the interlayer anion is selected from a monocarboxylic acid having the general structure (2)



a monoalkyl sulphate group having the general structure (3);



a monoalkyl ether sulphate group having the general structure (4)



an alkyl benzene sulphonate group having the general structure (5)



and mixtures thereof

where n is an integer of from 6 to 20  
and m is an integer of from 1 to 6;

(ii) a vegetable oil that is liquid at room temperature;  
and

(iii) a secondary thickener that is solid at room temperature.

DEFINITION OF THE INVENTION

5 The gel composition according to the invention, in its simplest form, comprises of a layered double hydroxide, a vegetable oil that is liquid at room temperature and a secondary thickener that is solid at room temperature. This composition has desirable occlusive properties.

10 The gel composition so formed will generally retain its gel-like characteristics over a wide temperature range for example from -15°C to +60°C.

The layered double hydroxide

15 With respect to structure (1) as defined above, x is preferably 0.15 to 0.4; more preferably 0.25 to 0.35 and z is preferably 0 to 4, more preferably 0 to 1.

20 Also with respect to structure (1), it is preferred that at least 70%, and most preferred at least 80%, of the interlayer anion (B) is selected from monocarboxylate, mono alkyl sulphate, monoalkyl ether sulphate, alkyl benzene sulphonate or mixtures thereof, the respective structure being as defined by structures (2), (3), (4) and (5).

25 Preferably the interlayer anion (B) is a monocarboxylic acid having the general structure (2).

30 The remaining interlayer anion component may be any inorganic or organic anion. Preferred are nitrate, carbonate, sulphate, chloride, citrate, benzoate and mixtures thereof.

35 Preferably gel compositions according to the invention comprise 1 to 40 wt%, more preferably 5 to 40 wt% and even more preferably 15 to 40 wt % of the layered double hydroxide.

### Synthesis of the layered double hydroxide

The layered double hydroxides may be prepared by several methods. Not wishing to preclude other routes, they may be precipitated from a solution containing a mixture of zinc/calcium/magnesium and aluminium salts (for example nitrates, chlorides, sulphates) by addition of sodium hydroxide or a similar base as detailed by Thevenot et al (Clays and Clay Minerals (1989) 5 396) or by direct reaction of a zinc/calcium/magnesium oxide slurry with an aluminium salt solution. The crystallinity and crystal size of the product may subsequently be increased by ageing the layered double hydroxide in its supernatant at temperatures up to 200°C. Moncarboxylate, suphonate, alkyl sulphate or alkyl ether sulphate ions may be introduced into the layered double hydroxide by ion exchange or using the partial decomposition-reformation procedure described by Dimotakis and Pinnavaia (Inorganic Chemistry (1990) 13, 2393).

It is preferred that the crystal size is small since smaller crystals provide better thickening properties. Especially preferred are crystals having a plate diameter of less than 0.2µm.

### Specific Examples of synthesis

#### 1. Zn/Al hydroxy nitrate

#### Preparation

94.5g of zinc oxide (ZnO) was weighed into a 1 litre polypropylene bottle and then slurried in 250ml water. 145.1g of aluminium nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was dissolved in 500ml of water and then added with stirring to the slurry. The bottle was capped, shaken vigorously, and then placed in a thermostat d oven at 90°C for 6 days. The solid was

filtered off, washed thoroughly with water, and then freeze dried. The material was finally equilibrated with water vapour at a water activity of 0.75.

5 Characterisation

Confirmed by XRD to be a layered double hydroxide with the Hydrotalcite structure. The basal spacing was 8.8Å (characteristic of a nitrate form material).

10

The Zn/Al ratio was found by XRF analysis to be 2.0.

IR indicated that Nitrate is the only anion present.

15

The water content was determined by thermal analysis and is consistent with the molar composition.



20

The water is labile and may vary slightly with storage.

TEM shows the crystals to be stacks of hexagonal plates of about 0.2µm diameter.

25

2. Zn/Al Hydroxy Laurate

Preparation

30

A solution of potassium laurate was first prepared by dissolving 28.43g of lauric acid and 8.34g of potassium hydroxide in 700ml of water and heating to about 70°C. 50g of Zn/Al hydroxy nitrate, prepared according to the method above, was placed in a 1l polypropylene bottle and the potassium laurate solution was added. The bottle was capped, shaken for 2 minutes and then placed in a thermostat d oven at 90°C for 18 hrs. Th solid was filtered off, washed thoroughly with hot wat r, and freeze

35

dried. The material was finally equilibrated with water vapour at a water activity of 0.75.

#### Characterisation

5

XRD showed the material was still a layered double hydroxide and that the basal spacing had increased from 8.8Å to 24Å.

10 Thermal analysis and elemental micro analysis gave the following percentages

% Residual Oxide (4 ZnO, Al<sub>2</sub>O<sub>3</sub>) = 42.51%

% Carbon = 29.68%

15

This is consistent with the molar composition



20 3. Zn/Al Hydroxy Stearate

#### Preparation

25 The procedure in (2) above was followed except that the lauric acid was replaced with 40.66g of stearic acid.

#### Characterisation

30 XRD showed the material was still a layered double hydroxide and that the basal spacing had increased from 8.8Å to 30.5Å.

Thermal analysis and elemental micro analysis gave the following percentages

35

% Residual Oxide (4 ZnO, Al<sub>2</sub>O<sub>3</sub>) = 36.55%

% Carbon = 33.72%

This is consistent with the molar composition



5      4.    Zn/Al Hydroxy Octanoate

Preparation

10      The procedure in 2 above was followed except that the lauric acid and potassium hydroxide were replaced with 23.8g of sodium octanoate.

Characterisation

15      XRD showed the material was still a layered double hydroxide and that the basal spacing had increased from 8.8Å to 19.5Å.

20      Thermal analysis and elemental micro analysis gave the following percentages

% Residual Oxide (4 ZnO, Al <sub>2</sub> O <sub>3</sub> )	= 48.20%
% Carbon	= 21.82%

25      This is consistent with the molar composition



30      5.    Mg/Al hydroxy nitrate

Preparation

35      46.8g of magnesium oxide (MgO) were weighed into a 1 litre polypropylene bottle and then slurried in 250ml water. 145.1g of aluminium nitrate (Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O) were dissolved in 500ml of water and then added with stirring to the slurry. The bottle was capped, shaken vigorously, and then



placed in a thermostated oven at 90°C for 5 days. The solid was filtered off, washed thoroughly with water, and then freeze dried. The material was finally equilibrated with water vapour at a water activity of 0.75.

5

#### Characterisation

Confirmed by XRD to be a layered double hydroxide with the Hydrotalcite structure. The basal spacing was 8.8Å

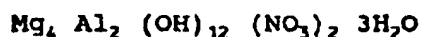
10

The Mg/Al ratio was found by XRF analysis to be 2.0.

IR indicated that Nitrate is the only anion present.

15

The water content was determined by thermal analysis and is consistent with the molar composition.



20

The water is labile and may vary slightly with storage.

TEM shows the crystals to be stacks of hexagonal plates of about 0.08µm diameter.

25

#### 6. Mg/Al hydroxy carboxylates

Carboxylate = Decanoate, Laurate, Myristate, Palmitate, Stearate.

30

#### Preparation

35

A solution of potassium carboxylate was first prepared by dissolving appropriate amount of carboxylic acid (see table below) and 10.61g of potassium hydroxide in 700ml of water and heating to about 70°C. 50g of Mg/Al hydroxy nitrate, prepared according to the method above, were placed in a 1L p lypropylene bottl and the potassium carboxylat solution

was added. The bottle was capped, shaken for 2 minutes and then placed in a thermostated oven at 90°C for 18 hrs. The solid was filtered off, washed thoroughly with hot water, and freeze dried. The material was finally equilibrated with water vapour at a water activity of 0.75.

Carboxylate	Weight of carboxylic acid
Decanoate	31.10g
Laurate	36.18g
Myristate	41.45g
Palmitate	46.62g
Stearate	51.63g

### Characterisation

Products analysed by XRD, thermal analysis, elemental micro analysis.

The analytical results for % residual oxide ( $4\text{MgO}, \text{Al}_2\text{O}_3$ ) and % carbon are given in the table below. These results are consistent with the composition



where p, q and r are given in the table below.

The basal spacing of the product (from XRD) is also given in the table.

Carboxylate	Basal spacing	% oxide	% carbon	p	q	r
Decanoate	21.5Å	34.66	24.33	1.6	0.4	4.6
Laurate	23.5Å	32.02	33.96	1.9	0.1	4.6
Myristate	26.0Å	29.97	36.82	1.9	0.1	4.6
Palmitate	28.0Å	28.48	40.08	1.8	0.2	5.1
Stearate	30.0Å	27.48	40.46	1.8	0.2	4.6

7. Mg/Al hydroxy octanoatePreparation

5 30.18g of sodium octanoate were dissolved in 700ml of water. 50g of Mg/Al hydroxy nitrate, prepared according to the method above, were placed in a 1L polypropylene bottle and the sodium octanoate solution was added. The bottle was capped, shaken for 2 minutes and then placed in a  
10 thermostated oven at 90°C for 18 hrs. The solid was filtered off, washed thoroughly with hot water, and freeze dried. The material was finally equilibrated with water vapour at a water activity of 0.75.

15 Characterisation

Products analysed by XRD, thermal analysis, elemental micro analysis.

20 The analytical results were as follows:

% oxide (4MgO, Al <sub>2</sub> O <sub>3</sub> )	= 37.78
% carbon	= 24.30

25 These results are consistent with the composition



The basal spacing of the product (from XRD) was 19.5Å.

30

The Vegetable Oil

Suitable compounds are liquid at room temperature (20°C).

35

The vegetable oil may be chosen from:

- Rapeseed oil
- Coconut oil
- 5 Cottonseed oil
- Groundnut oil
- Corn oil
- Olive oil
- Palm oil
- 10 Palm kernel oil
- Sesame seed oil
- Sunflower seed oil
- Avocado pear oil
- Neem oil
- 15 Safflower oil
- Soya bean oil
- Thistle seed oil
- Cocobutter
- Shea butter
- 20 Almond oil
- Rice bran oil

- Preferably gel compositions according to the invention comprise 50 to 90 wt % of the composition, more preferably
- 25 60 to 80 wt % of the composition and even more preferably 70 wt % of the composition of the vegetable oil.

The Secondary Thickener

- 30 The secondary thickener is solid at room temperature. Such secondary thickeners must also be compatible with, and able to form some structure in, the lipophilic organic compound disclosed above.
- 35 Preferred secondary thickeners may be selected from plant and animal fats, waxes and oils, paraffinic hydrocarbons; silicone oils; aliphatic and aromatic esters; higher

alcohols and thers; polyethylene and copolymers of polyethylene and mixtures thereof.

5 Examples of the preferred secondary thickeners include  
sucrose fatty acid polyesters (for example sucrose  
octaisostearate, sucrose octa-2-ethylhexanoate, those  
derived from palm and palmkernal oil mixtures, soyabean  
oil, soyabean and palm oil mixtures, palm oil, coconut oil  
and mixed fish oils); high melting point triglycerides (eg.  
10 hardened palm oil, hardened rape seed oil); Candeulla wax;  
jojoba wax; beeswax, paraffin waxes, petroleum waxes,  
ceracin wax; polyethylene homopolymers (such as A-C  
polyethylene 1702 (trademark), A-C polyethylene 617  
(trademark), A-C polyethylene 6 (trademark)); and  
15 polyethylene vinyl acetate copolymers (such as A-C  
ethylene-vinyl acetate 405 (trademark), A-C ethylene vinyl  
acetate 400 (trademark)).

20 Preferably gel compositions according to the invention  
comprise 1 to 40 wt % of the composition, even more  
preferably 10 to 30 wt % of the composition of the  
secondary thickener.

#### OTHER INGREDIENTS

25 The gel composition according to the invention can  
optionally comprise other ingredients to provide additional  
skin or hair benefits.

30 Such ingredients include healing agents, humectants,  
thickeners, antioxidants, stabilisers, film formers,  
emulsifiers, surfactants, sunscreens, preservatives,  
perfumes and colourants.

35 The gel composition according to the invention can also  
comprise other ingredients conventionally used in cosmetic  
products which are suited to topical application to human

skin or hair.

Other ingredients, when present, can form up to 50% by weight of the composition and can conveniently form the balance of the gel base.

#### Process for preparing the gel composition

The invention also provides a process for the preparation of a gel suitable for topical application to skin or hair, which comprises the step of blending a layered, double hydroxide as herein defined, with a vegetable oil and a secondary thickener compound as herein defined.

According to a preferred embodiment of the process for preparation of the gel, the layered double hydroxide and vegetable oil are heated together with stirring to dissolve the layered double hydroxide. The suspension is then subjected to high shearing forces until thickening has occurred.

When polyethylene is used as the secondary thickener it is preferred to stir the suspension on cooling through the cloud point to ensure efficient gelling.

#### Use of the Composition

Gel compositions according to the invention can be used for providing an occlusive layer on human skin, to reduce moisture loss, following topical application thereto of the gel composition. The skin can thereby be protected from adverse climatic conditions, for example from excessive exposure to sun and wind, or from detergent damage, for example that following immersion of the hands in aqueous detergent solution when washing dishes or clothes.

In use, a small quantity of the gel composition, for

example from 1 to 5g, is applied to the skin or hair from a suitable container or applicator and, if necessary, it is then spread over and/or rubbed into the skin or hair using the hand or fingers or a suitable spreading device.

5

#### Product form and packaging

The gel composition of the invention can be formulated as a soft solid or jelly-like product having the rheological and other physical properties as herein defined, and it can be packaged in a suitable container to suit its viscosity and intended use by the consumer. For example, the gel composition can be stored in a deformable tube or in a lidded jar.

15

The invention accordingly also provides a closed container containing the gel composition as herein defined.

#### Physical properties of the gels

20

##### (i) Viscosity Measurement

Viscosity measurements were made using a Brookfield Viscometer: a multispeed rotational viscometer calibrated to measure the torque required to rotate a spindle, attached to a Beryllium copper spring, at constant speed. The measurements were taken using a Brookfield model RVT, at a speed of 20 r.p.m., using a T-bar spindle D (cross bar length 2.1cm), at room temperature (ca 23°C) and using a Helopath stand.

30

#### Procedure for Taking Measurements

The T-bar spindle D was attached to the viscometer coupling and the instrument levelled using an internal spirit gauge. The spindle was carefully inserted into the sample, avoiding trapping air below the spindle surface, and the

35

locking lever depressed whilst the motor was started to rotate the spindle. Slow release of the locking lever allows a pointer to move on the viscosity scale and this is given 5-10 seconds to steady before locking in position. The motor was switched off and the reading on the scale taken. From this:

$$\text{VISCOSITY} = \text{READING} \times \text{SPINDLE FACTOR}^*$$

\* factor for spindle D = 1000

Four measurements were taken for each sample and an average recorded.

#### (ii) Occlusivity

The gel composition according to the invention have a significant Occlusivity Value if secondary thickeners are included in the composition, such compositions may be employed like petrolatum, to provide an occlusive layer on skin or elsewhere on the body surface. For such a use it is preferred that the gel composition will have an Occlusivity Value of at least 20%, as measured by the Occlusivity Value Test. Details of how this test is performed are given below.

#### Occlusivity Value Test

In view of the wide variation in the characteristics and properties of human skin, as seen amongst a group of individuals of differing ages, races and habitat, it is necessary to provide a standard in vitro test which is readily reproducible, in order to measure the occlusivity of the gel composition.

An empirical test has accordingly been devised using a standard viscose cellulose film, namely Visking dialysis



tubing available from Medicell International Ltd. as a substitute for human skin. This film has a molecular weight cut-off of from 12,000 to 14,000.

- 5 In this test, the occlusivity of a film of the oleogel to the passage of water vapour applied to the dialysis film is measured in a standard manner as follows:

Preparation of occlusivity cell

10

A 5ml beaker, for example a Dispo beaker available from American Scientific Products, the diameter of the open end of which is 25mm (i.e. an area of  $5\text{cm}^2$ ), is used to provide an occlusivity cell.

15

1ml distilled water is introduced into the beaker and a film of Visking dialysis tubing is stretched across the open end of the beaker and fixed in place with adhesive, for example Assembly Aid Adhesive (3M).

20

The rate of water loss through the Visking film at  $20^\circ\text{C}$ , at atmospheric pressure and at 50% external relative humidity, is determined by measuring the decrease in weight of the beaker with time using a Sartorius 4503 microbalance, with a D to A converter feeding the output to a chart recorder.

25

After a steady-state water loss rate has been established, a product whose Occlusivity Value is to be tested, i.e. the gel composition of the invention is applied as a film to the surface of the Visking dialysis tubing. When the test substance is liquid or a soft solid, it can be applied using a plastic-gloved finger. When the test material is a solid, it is necessary first to melt it as it is applied to the surface of the Visking dialysis film.

30

35

The new steady-state water loss rate, under the same physical conditions of pressure, temperature and relative

humidity, is then recorded after excess water from the product has been lost.

Occlusivity of the product film (ie. the gel composition) is then calculated as:

$$\% \text{ occlusivity} = 1 - \frac{\text{water loss rate with product}}{\text{water loss rate without product}} \times 100$$

All water loss rates are corrected for the relatively small rate of water loss through the walls of the beaker (if any). This is determined by measuring the water loss from a beaker where the Visking film is replaced with impermeable aluminium foil.

Occlusivity is normally determined 4 times for each sample. For each measurement, the sample loading is determined from the increase in recorded weight immediately after application to the Visking film of the composition of the invention. Since the loading is not reproducible precisely, a straight line is fitted to a loading versus occlusivity plot (by linear regression) and the occlusivity at a typical consumer product loading of 10g/sq m is then interpolated. In each case, the occlusivity is approximately linearly dependent on the loading for the range covered.

The occlusivity is then expressed as an arithmetic mean of the 4 determinations  $\pm$  2 standard errors for 95% significance.

Experience has shown that about 10mg of the product applied to the Visking film is sufficient to provide an occlusive layer; without an occlusive layer, the film will normally transmit about 25g water vapour/m<sup>2</sup>/hr.

EXAMPLES

The invention is illustrated with reference to the following examples in accordance with the invention.

5

Examples 1-4, Comparative Examples A-D

10 The layered double hydroxide powder was suspended in rapeseed oil and heated on a hot-plate to 90°C with stirring. A shearing aid, polyoxyethylene-(4)-lauryl alcohol (0.05% based on the powder used) was then added and the suspension was heated to about 120°C with stirring until starting to foam slightly. Without cooling further the suspension was then subjected to high shearing forces  
15 in a Silverson mixer for about 1-5 minutes until thickening has occurred. Where secondary structurants are used (examples 1-2), these are added to the oil and heated, with stirring, until molten before addition of the layered double hydroxide. For example 3 the polyethylene/vinyl  
20 acetate co-polymer was added with the hydrotalcite and the mixture was stirred through the cloud point (~85°C) of the polyethylene/vinyl acetate co-polymer when cooling to ensure efficient gelling.

25 Compositions and occlusivity results are shown in Table 1.

nm = not measured

30 Results clearly show the increased occlusivity on addition of the secondary thickener.

Table 1

Composition ingredient (%)	Example									
	1	2	3	4	A	B	C	D		
Zn/Al laurate layered double hydroxide	20	15	15	0	0	0	30	40		
Mg/Al laurate layered double hydroxide	0	0	0	14	30	40	0	0		
Rapeseed oil	40	75	80	68	70	60	70	60		
Sucrose polyester 260-R-7	40	0	0	0	0	0	0	0		
White Beeswax	0	10	2.5	18	0	0	0	0		
Polyethylene/vinyl acetate	0	0	2.5	0	0	0	0	0		
Occlusivity ‡	33	38	28	23	NEGLECTIBLE AT Standard loading of 10g/m					
viscosity (cp)	>100000	38250	37500	nm	64066	nm	29000	nm		

5

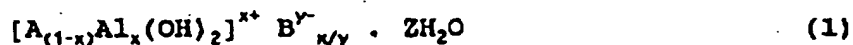
10

15

CLAIMS

1. An occlusive gel composition comprising:

- 5 (i) a layered double hydroxide having the general structure (1).



- 10 where A is a calcium, magnesium or zinc ion  
B is an interlayer anion  
y is a charge on the anion  
x is 0.1 to 0.5  
z is 0 to 100

- 15 providing that at least 50% of the interlayer anion is selected from a monocarboxylic acid having the general structure (2);



a monoalkyl sulphate group having the general structure (3);



a monoalkyl ether sulphate group having the general structure (4);



an alkyl benzene sulphonate group having the general structure (5);



and mixtures thereof

wher        n is an integer of from 6 to 20  
and        m is an integer of from 1 to 6; and

5        (ii) a vegetable oil that is liquid at room temperature,  
and

(iii) a secondary thickener that is solid at room  
temperature.

10       2. A gel composition according to claim 1 comprising 1-40  
wt % of the composition of the layered double hydroxide. #

15       3. A gel composition according to any preceding claim  
comprising 5 to 40 wt % of the composition of the layered  
double hydroxide.

20       4. A gel composition according to any preceding claim  
comprising 15 to 40 wt % of the composition of the layered  
double hydroxide.

25       5. A gel composition according to any preceding claim  
comprising 50 to 90 wt % of the composition of the  
vegetable oil.

30       6. A gel composition according to any preceding claim  
comprising 60 to 80 wt % of the composition of the  
vegetable oil.

35       7. A gel composition according to any preceding claim  
wherein the secondary thickener compound is selected from  
plant and animal fats, plant and animal waxes, plant and  
animal oils, paraffinic hydrocarbons, silicone oils,  
aliphatic and aromatic esters, higher alcohols and ethers,  
polyethylene and copolymers of polyethylene and mixtures  
thereof.

8. A gel composition according to any preceding claim comprising 1 to 40 wt % of the composition of the secondary thickener.
- 5 9. A gel composition according to any preceding claim comprising 10 to 30 wt % of the composition of the secondary thickener.
- 10 10. The use of a gel composition according to any preceding claim to provide an occlusive layer on human skin to reduce moisture loss, following topical application thereto of the gel composition.